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Predicted effectiveness of in-situ activated carbon amendment for field sediment sites with variable site- and compound-specific characteristics

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ABSTRACT

A growing body of evidence shows that the effectiveness of in-situ activated carbon (AC) amendment to treat hydrophobic organic contaminants (HOCs) in sediments can be reliably predicted using a mass transfer modeling approach. This study analyzes available field data for characterizing AC-sediment distribution after mechanical mixing of AC into sediment. Those distributions are used to develop an HOC mass transfer model that accounts for plausible heterogeneities resulting from mixing AC into sediment. The model is applied to ten field sites in the U.S. and Europe with 2-3 representative HOCs from each site using site- and HOC-specific model parameters collected from the literature. The model predicts that the AC amendment reduces the pore-water HOC concentrations by more than 95% fifteen years after AC deployment for 18 of the 25 total simulated cases when the AC is applied at doses of 1.5 times sediment total organic carbon content with an upper limit of 5 dry wt%. The predicted effectiveness shows negative correlation with the HOC octanol-water partitioning coefficients and the sediment-water distribution coefficients, and positive correlation with the effectiveness calculated based on equilibrium coefficients of sediment and AC, suggesting the possibility for use of the values for screening-level assessments.

Highlights

- The model accounts for the heterogeneity of AC distribution in field applications
- AC amendment effectiveness is predicted for ten sediment sites
- An HOC mass transfer model and calibrated parameters provide reliable predictions

- AC amendment is predicted to be effective for most sites
- K_{ow} , K_d , and equilibrium-based calculations are useful indicators

Keywords: Activated carbon amendment; Mass transfer model; Sediment remediation;
In-situ treatment; Hydrophobic organic contaminants

1. Introduction

In-situ activated carbon (AC) amendment is a promising technology to treat hydrophobic organic contaminants (HOCs) in sediments. The bioavailability and mobility of HOCs are effectively reduced by AC amendment as the HOCs in the sediment are sorbed to AC through a series of mass transfer processes [1-4]. Laboratory studies employing well-mixed slurry tests as well as extended-duration column experiments have validated the effectiveness of the treatment for various types of HOCs [1, 5-8]. Further, pilot scale studies have demonstrated the proof-of-concept of the technique for a tidal mudflat [9-11], river bed sediment [12], and deep water sediment sites [13].

Despite the potential of the AC-amendment technique to replace or supplement conventional sediment treatment options such as dredging and capping, it is still rarely implemented at full scale. Hence, one of the barriers for the field application of AC-amendment is the limited knowledge of the effectiveness of the technique under field conditions [10, 14]. Currently, there are only a few sites where in-situ AC amendment has been implemented at a full scale [15]. In these sites, the AC was deployed as a thin layer cap in lieu of active mechanical mixing of AC with sediment [15]. The effectiveness of the treatment is found to vary for different compounds and site conditions [9, 12, 13]. The AC-amendment treatment effectiveness depends on the interaction of various factors such as HOC properties, HOC partitioning among sediment, AC, and pore-water, AC sorption and sediment desorption kinetics, AC dose, AC grain size and AC distribution heterogeneity [5, 7, 8, 16]. This makes it difficult to quantify the

contribution of each factor using simple expressions. The long-term effectiveness is a concern due to the lack of the field monitoring data for extended time periods [14].

An HOC mass transfer model has been developed to enable the prediction of the long-term effectiveness of in-situ AC amendment, i.e., 10-20 years or more, under various field conditions. The model was initially developed by Werner et al. [17] for continuously-mixed sediment slurry systems and subsequently modified for relevance to field conditions [4, 10, 18]. The model has been successfully applied for laboratory and pilot-scale studies. The model has been shown to work well under different situations to describe the mechanism of the HOC mass transfer processes among AC, sediment, and pore-water by sophisticated modeling techniques and calibrated parameters.. The model reasonably predicted the pore-water concentrations of polychlorinated biphenyls (PCBs) following pilot-scale AC amendment at Hunters Point Shipyard, San Francisco Bay [10]. In laboratory column studies, the model was shown to quantitatively reproduce the varying effectiveness of the treatment for polycyclic aromatic hydrocarbons (PAHs) observed in the experiments, accounting for the compound and sediment properties, AC application scenarios, and pore-water flow regimes [4]. Recently, the model was modified to include the bioturbation effects by freshwater worms and predictions matched well with the experimental data for a dichlorodiphenyltrichloroethane (DDT) metabolite in microcosm experiments [19]. With additional ongoing studies that combine modeling and observed results at laboratory and pilot scales, there is a growing body of evidence that demonstrate the reliability of the HOC mass transfer model to predict the effectiveness of AC amendment.

To use the HOC mass transfer model for decision-making in support of full-scale applications of in-situ AC amendments, the heterogeneity of AC distribution in sediment under field conditions needs to be incorporated to the model. The AC distribution heterogeneity plays a significant role in the overall HOC mass transfer process occurring within AC-amended sediment and thus impacts the effectiveness of the treatment [4, 10]. Poor distribution results in longer average diffusion distances between HOC molecules released from sediment and the surface of AC particles. In the field, it is difficult or practically infeasible to homogeneously distribute AC into the target mixing depth of the sediment because of the scale issue and the difficulty to control the mixing depth [9, 11].

In addition, estimation methods simpler than HOC mass transfer modeling are needed to allow easy and straightforward assessment of the feasibility of the treatment at a screening level. The mass transfer model is relatively sophisticated and may require calibration with site-specific model input parameters through laboratory measurements [4]. Therefore, it would be desirable to develop simpler methods that can be used at a screening level, while the HOC mass transfer model may serve as a prediction tool when the feasibility of in-situ AC amendment is extensively evaluated.

In this study, an HOC mass transfer model is developed by applying the previously described modeling concepts for HOC mass transfer in AC-amended field sediment with incorporation of the heterogeneity of AC distribution. Scenarios are analyzed by employing AC distribution heterogeneities observed in previous field studies. The developed model is applied for ten study sites in the U.S. and Europe. The effectiveness of in-situ AC amendment predicted by the model is analyzed along with relevant site-specific variables or simpler models to identify the potential of those

variables or models as indicators for the feasibility of the treatment. Correlations among the HOC mass transfer model-predicted short- and long-term effectiveness and the potential indicators are assessed.

2. Methods

2.1. HOC mass transfer modeling concept

The concepts for the theory underpinning the HOC mass transfer model are described in detail elsewhere [4, 17, 18]. The AC-amended sediment is conceptualized as comprising four different domains, two sediment domains with fast- and slow-HOC-releasing kinetics, the AC, and the sediment pore-water. As discussed in Werner et al. [17], the HOC movement within each solid-phase domain (i.e., sediment and AC) is calculated using an intra-particle diffusion model applying local equilibrium of the outer boundary with adjacent pore-water. To simulate a field scenario in which AC is mixed into sediment by mechanical devices and the AC-amended sediment remains undisturbed thereafter, the model is comprised of a well-mixed module for a short period (on the order of a minute or two) followed by an unmixed module for an extended time period (on the order of a decade). For the well-mixed module, the model system is assumed to be continuously mixed with a spatially invariant concentration in pore-water and concentration profiles for the solid-phase domains. The overall HOC mass balance in the well-mixed module is described as

$$V_w \frac{dC_w}{dt} = -V_s \frac{d}{dt} \left[\frac{3}{R_s^3} \left\{ \int_0^{R_s} r^2 S_{s,fast}(r) dr + \int_0^{R_s} r^2 S_{s,slow}(r) dr \right\} \right] \quad (1)$$

$$- V_{AC} \frac{d}{dt} \left[\frac{3}{R_{AC}^3} \int_0^{R_{AC}} r^2 S_{AC}(r) dr \right]$$

where C_w is the HOC pore-water concentration (ng cm^{-3}); V_w , V_s , and V_{AC} are the volumes (cm^3) of pore-water, sediment, and AC, respectively; R_s and R_{AC} are the radii (cm) of sediment and AC, respectively; r is the distance (cm) from the center of each spherical particle; and $S_{s,fast}(r)$, $S_{s,slow}(r)$, and $S_{AC}(r)$ are the local volumetric HOC concentrations (ng cm^{-3}) at a radial distance of r for fast- and slow-HOC releasing sediment sorption domains, and AC, respectively. The outcome of the well-mixed module is used as initial conditions in the unmixed module.

For the unmixed module, a three-dimensional model system is constructed by stacking small cubes sized just large enough to accommodate a single AC particle, e.g., 1.5 times the AC diameter. Each cube contains the pore-water phase and the two sediment domains with its own concentration and concentration profiles, respectively. AC particles are assigned to some of the cubes replacing the equivalent volume of sediment. Depending on the presence or absence of AC particles in the cubes, HOC concentration gradients develop among neighboring cubes over time. According to the concentration gradients developed in the pore-water domain, each cube exchanges HOCs with neighboring cubes by molecular diffusion. The movement of pore-water itself is neglected in this paper because previous studies showed that the transport of HOCs by pore-water advection and fluid dispersion did not significantly facilitate the overall HOC mass transfer within a relevant range of pore-water flow velocities [4, 8]. The overall HOC mass balance for the unmixed module is expressed as

$$\begin{aligned}
& V_w \left[\frac{dC_w}{dt} - \tau \cdot D_{aq} \nabla^2 C_w \right] \\
& = -V_s \frac{d}{dt} \left[\frac{3}{R_s^3} \left\{ \int_0^{R_s} r^2 S_{s,fast}(r) dr + \int_0^{R_s} r^2 S_{s,fast}(r) dr \right\} \right] \\
& \quad - V_{AC} \frac{d}{dt} \left[\frac{3}{R_{AC}^3} \int_0^{R_{AC}} r^2 S_{AC}(r) dr \right]
\end{aligned} \tag{2}$$

where D_{aq} is the aqueous diffusivity ($\text{cm}^2 \text{s}^{-1}$) of the HOC; and τ is the tortuosity factor (dimensionless) for sediment inter-particle pore, which is set equal to the sediment inter-particle porosity.

2.2. Activated carbon (AC) distribution heterogeneity analysis

To incorporate the potential heterogeneity in AC distribution as a result of mechanical mixing in the field, the data for AC dose measurements for a pilot-scale study at Hunters Point Shipyard, CA [9, 10] are reanalyzed for application to the mass transfer model. To our knowledge, this is the only work that reported comprehensive data on AC distribution for a pilot-scale study employing mechanical mixing of sediment and AC.

As described by Cho et al. [9], a rotovator device was applied to one of the test plots to mechanically mix AC into sediment with a target mixing depth of 30 cm. Six and eighteen months after the mixing, five 30 cm sediment cores each (ten cores in total) were taken. The cores were divided into six 5-cm sections and a composite sample from each section was analyzed for AC dose as % dry weight of sediment. From these data, the average AC dose for the entire core was calculated for each of the ten cores. The normalized AC dose for each section of the core was then calculated as

Normalized section AC dose (3)

$$= (\text{Measured section AC dose}) / (\text{Avg. AC dose for entire core})$$

To observe the AC distribution heterogeneity at a smaller scale, i.e., on the order of a few millimeters, thirty 100 mg samples each were collected from two 5-cm-long sediment cores taken at the sediment depth of 5-10 cm from the same test plot [10]. These previously reported millimeter-scale AC dose data were analyzed to calculate relative standard deviation (%) within the 5 cm sections.

2.3. Study sites and model input parameters

Ten sediment sites in the U.S. and Europe were selected to study the effectiveness of in-situ AC amendment using the HOC mass transfer model. These sites were selected based on the availability of site- and HOC-specific model input parameters. The site characteristics and contaminant information were obtained from previous reports in the literature for each site [1, 4, 6, 7, 16, 18-22] and are summarized in **Table A.1 in Appendix A**. The study sites exhibit a range of sediment total organic carbon (TOC) and black carbon (BC) contents, types of major HOCs of concern (PCBs, PAHs, and DDTs), HOC release rates, and other sediment characteristics. Two or three representative HOCs are selected from each site based on their relative abundance and the availability of the HOC mass transfer model input parameters from the literature.

The input parameters comprise site- and HOC-specific characteristics including initial pore-water HOC concentrations, sediment-water distribution coefficients, sediment desorption parameters, AC-water partitioning coefficients, and apparent AC intra-particle

diffusion coefficients. These are summarized in **Table A.2 in Appendix A**. Intrinsic HOC properties including octanol-water partitioning coefficients and aqueous diffusivity for the model HOCs are shown in **Table A.3**. Physicochemical properties of sediment and AC, used as model input parameters, are summarized in **Table A.4**.

It is assumed that the same AC is used for all sites with a particle size range of 75-300 μm (geometric mean radius of 75 μm). The average AC dose for the whole model system is set at 1.5 times the sediment TOC with an upper limit of 5% sediment dry weight. A well-mixed AC dose of 1-2 x TOC has been shown to be effective for controlling HOC bioavailability in laboratory experiments [5, 7]. Although still not completely understood as to mechanisms, several studies report adverse effects of AC amendments on sediment biota at high AC dose [23-27]. Based on approximate AC doses at which adverse effects are not observed in those studies, 5% sediment dry weight is chosen as a maximum AC dose for assessment in this work.

2.4. Model execution

The HOC mass transfer model developed in this study, including incorporation of heterogeneity in the AC distribution within the sediment, was run for the model HOCs for each site. This resulted in 25 simulation runs. For the unmixed module, the cube side-lengths were specified as 225 μm , which were three times the geometric mean radius of AC. The three-dimensional model system had a depth of 15 cm and a horizontal dimension of 0.225 cm x 0.225 cm (10 x 10 cubes). The vertical dimension represented the potential mixing depth of AC with sediment, which encompasses the bioactive layer

of sediment [12]. The horizontal dimension is minimized to save computation time while not affecting the model outputs.

The mass transfer model was run for a simulation time of 1 min for brief mechanical mixing using the mixed module followed by a simulation time of 15 years using the unmixed module for AC-sediment contact during a prolonged stagnant phase. The model outputs were the average pore-water HOC concentration, and average HOC mass fractions residing in sediment and AC. The predicted average pore-water HOC concentrations after 3 and 15 years of contact during the stagnant phase were tabulated for each simulation run for further analyses. Three and fifteen years of stagnant contact were selected to produce the data representing short- and long-term effectiveness, respectively.

2.5. Simpler models for indicators of HOC mass transfer

Indicators that can be derived from models simpler than the HOC mass transfer model have the potential applicability to determine the feasibility of in-situ AC amendment at a screening level. These indicators were studied for correlation with the simulation results of the HOC mass transfer model at the study sites. These values may be used for a preliminary assessment along with other potential descriptors of HOC mass transfer such as octanol-water partitioning coefficients (K_{ow}), sediment-water distribution coefficients (K_d), AC-water partitioning coefficients (K_{AC}), sediment TOC and BC contents

The fractions of 30-d HOC desorption from sediment were developed as a single measure of HOC desorption kinetics from sediment. Using the three model input parameters involved in sediment desorption, fast- and slow-HOC-releasing rates (k_{fast} and k_{slow} , respectively; d^{-1}), and the fraction of slow-releasing HOC in sediment (f_{slow} ; dimensionless), the fraction of 30-d desorption was calculated as [17]

$$\frac{m(t)}{m_{tot}} = 1 - f_{slow} \left[\frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-k_{slow} n^2 \pi^2 t) \right] - (1 - f_{slow}) \left[\frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-k_{fast} n^2 \pi^2 t) \right] \quad (4)$$

where $m(t)/m_{tot}$ is the mass fraction of HOC desorption from sediment for time $t=30$ days.

The relative pore-water concentration at equilibrium, $(C_w/C_{w0})_{eq}$, represents the endpoint the effectiveness of AC amendment for a given site, a target HOC, and an AC dose. Using the site-specific partitioning coefficients of the target HOCs for sediment and AC, and the AC dose (% sediment dry weight), the relative pore-water concentration under equilibrium HOC partitioning between sediment and AC was calculated as

$$(C_w/C_{w0})_{eq} = \frac{K_d \times \{1 + (AC \text{ dose})/100\}}{K_d + K_{AC} \times \{(AC \text{ dose})/100\}} \quad (5)$$

where K_d is the sediment distribution coefficient ($\text{cm}^3 \text{g}^{-1}$) and K_{AC} is the AC-water partitioning coefficient ($\text{cm}^3 \text{g}^{-1}$). Note that for this study the AC dose was defined as the amount of AC added to the original sediment, not the dose of the sediment-AC mixture after AC amendment. A similar approach was employed in Beckingham and Ghosh [12] to compare the treatment effectiveness calculated based on HOC equilibrium and the effectiveness observed in a pilot-scale field study.

3. Results and Discussion

3.1. Incorporation of AC distribution heterogeneity into the HOC mass transfer model

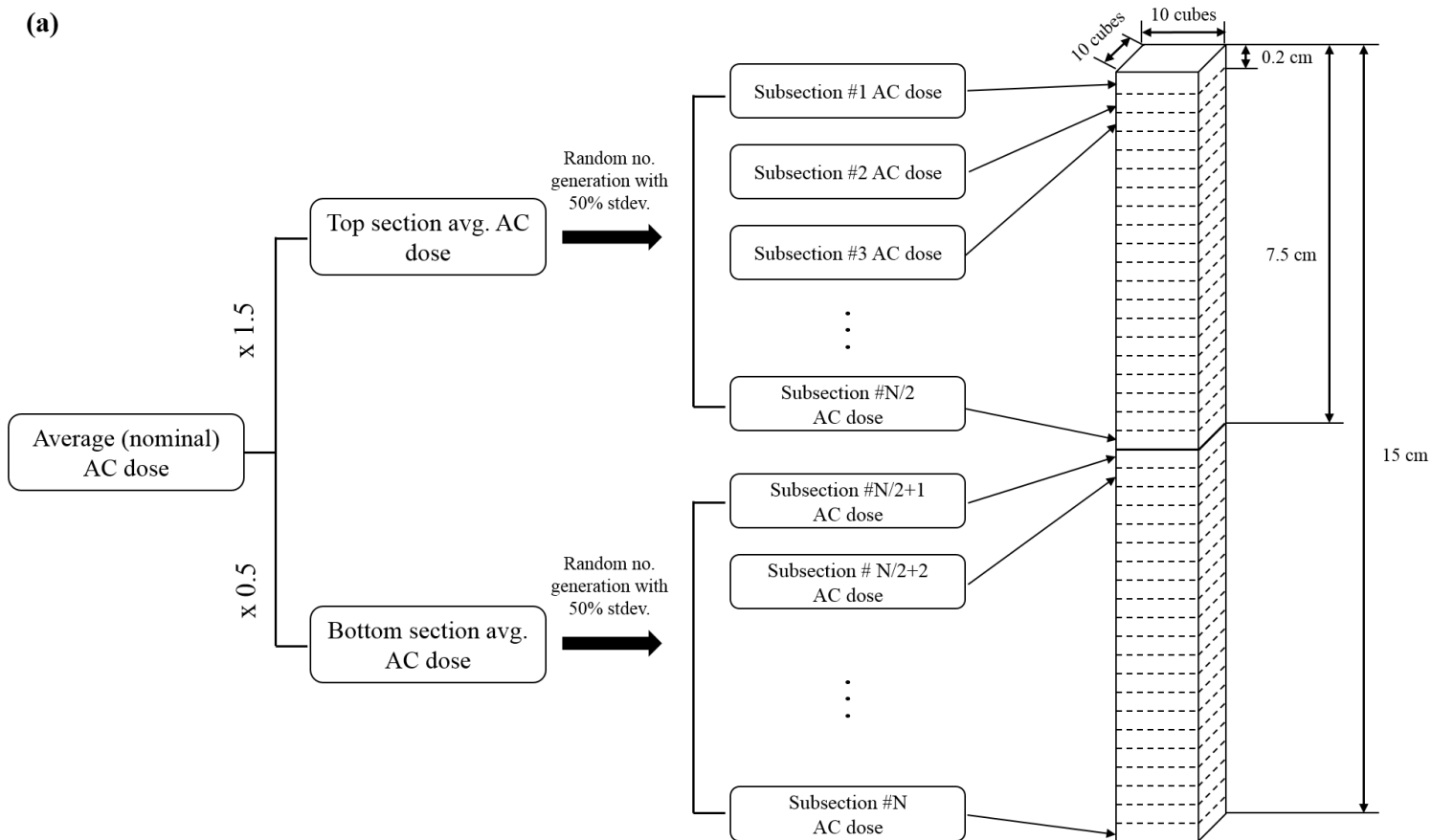
The normalized AC dose for 5-cm sections of sediment cores ($n=10$) obtained from the Hunters Point Shipyard pilot-scale study is shown in **Fig. A.1 in Appendix A**. The average normalized AC doses for the first 0-15 cm and the next 15-30 cm core depth samples are approximately 1.5 and 0.5, respectively. Similar depth-dependent AC dosages were reported at a pilot study site at Grasse River, NY [12]. Accordingly, to represent the possible depth-dependent variation of AC dose by insufficient AC mixing in the field, the whole depth for modeling (i.e., 15 cm) is divided into halves, and the average AC dose for the whole depth is multiplied by a factor of 1.5 and 0.5 for the first and second halves, respectively.

The analysis of the millimeter-scale AC dose data from the Hunters Point Shipyard study ($n=30$ each for two sediment cores) resulted in an average relative standard deviation of 50% among the subsamples. To apply the heterogeneity of local AC dose, the halved sections of the whole depth are further divided into 2-mm-subsections in the model system. Using the AC doses for the top and bottom sections and a relative standard deviation of 50%, the AC doses for the 2-mm-subsections are randomly generated using a MATLAB function. In each subsection, the AC particles are assumed to be randomly distributed. The AC distribution heterogeneity at the particle-scale (i.e., on the order of 10^{-1} millimeter or less) does not substantially affect the predicted effectiveness of AC amendment after more than 3 years of stagnant contact.

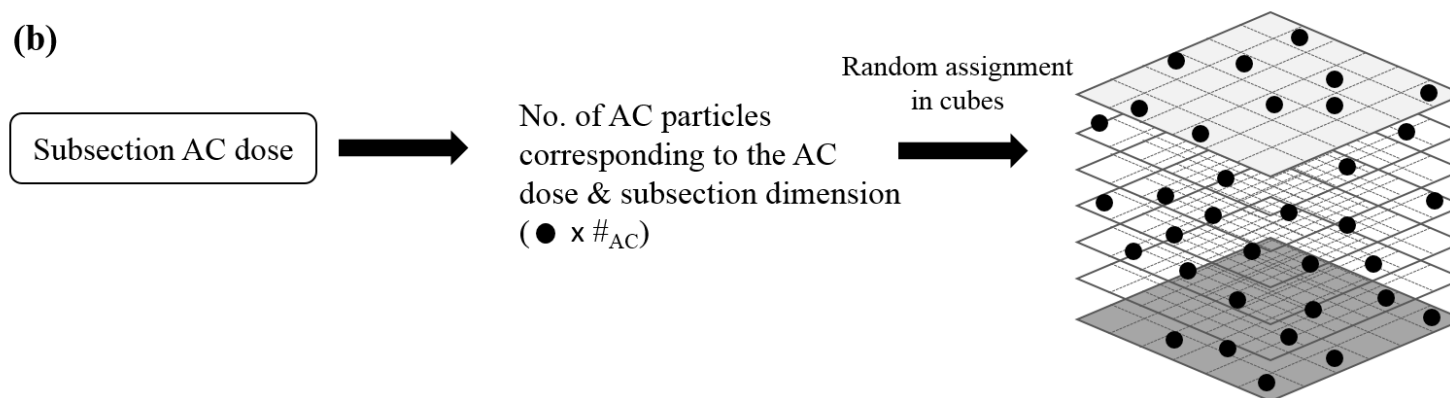
The overall scheme for the AC particle distribution in the model system developed in this study is depicted in **Fig. 1**. The simulation results for the new model applying the heterogeneous AC distribution fit reasonably well with the field monitoring results for Hunters Point pilot-scale study reported in Cho et al. [10] (see **Fig.A.2 in Appendix A**). The slight increase in the sediment pore-water PCB concentrations observed in the field data as opposed to the modeling results is likely a result of the inflow of PCBs from the adjacent, untreated plots as discussed in detail in Cho et al. [10].

The HOC mass transfer model developed in this study should be further validated with a larger number of field studies, preferably at sites with full-scale implementation of in-situ AC amendment. In-situ AC amendment employing mechanical mixing of AC into sediment has yet to be applied in the field at a full scale. Efforts are also needed to improve knowledge on the AC mixing heterogeneity following mechanical mixing of AC into sediment with different types of mixing devices, their dimension, and the mixing duration as variables. For the following discussion, it is assumed that the HOC mass transfer model developed in this study will reasonably predict the effectiveness of in-situ AC amendment for the studied sites.

Fig. 1. The overall scheme for the AC particle distribution in the HOC mass transfer model system developed in this study to represent field distribution heterogeneity. (a) Determination of AC dose for each section and subsection, (b) assignment of AC particles in each subsection.



(b)



3.2. Simulated effectiveness of in-situ AC amendment

The simulated percent reductions in pore-water concentrations, $(1-C_w/C_{w0}) \times 100$ (%), compared to the initial value 3 and 15 years after AC deployment relative to the initial concentration ($(C_w/C_{w0})_{3yr}$ and $(C_w/C_{w0})_{15yr}$, respectively) are shown in **Table 1**.

Table 1. Summary of the HOC mass transfer modeling results for the ten study sites.

The results are shown as the percent reduction in pore-water concentrations calculated by $(1-C_w/C_{w0}) \times 100$ (%).

Study site and location	Compound	Short term (3 yr)	Long term (15 yr)	Endpoint (equilibrium)
Site#1: Hunters Point Shipyard	PCB 153	77.1%	96.6%	99.6%
	PCB 180	61.4%	88.3%	99.6%
Site#2: Lake Hartwell	PCB 52	99.5%	99.8%	99.9%
	PCB 101	94.4%	99.6%	99.9%
Site#3: Crab Orchard Lake	PCB 52	99.7%	99.8%	99.9%
	PCB 118	82.4%	98.5%	99.9%
	PCB 138	74.5%	97.5%	99.9%
Site#4: Milwaukee River, location 1	PCB 28	93.2%	98.3%	99.3%
	PCB 49	86.0%	89.1%	91.9%
	PCB 101	67.7%	78.1%	83.0%
Site#5: Milwaukee River, location 2	PCB 28	95.3%	99.0%	99.5%
	PCB 49	82.5%	87.6%	91.5%
	PCB 101	59.5%	70.8%	78.2%
Site#6: Grasse River	PCB 26	98.7%	99.6%	99.7%
	PCB 47	95.0%	98.1%	98.8%
	PCB 91	85.1%	90.3%	94.1%
Site#7: River Tyne	PHEN	99.0%	99.6%	99.7%
	FLUA	98.0%	99.8%	99.9%
	BaP	95.9%	98.8%	93.8%

Site#8: Undisclosed, petroleum-impacted site	PYR	98.4%	99.6%	99.9%
	BaP	93.3%	98.7%	99.5%
Site#9: Lauritzen Channel	p,p'-DDT	26.8%	34.0%	86.7%
	p,p'-DDD	90.0%	98.7%	99.5%
Site#10: Undisclosed, freshwater lake	p,p'-DDD	99.2%	99.8%	99.9%
	p,p'-DDE	97.7%	99.8%	99.9%

In most cases, the simulation results show substantial reduction in the sediment pore-water concentrations in the short term (3 years) as well as in the long term (15 years). Among the total of 25 simulated cases at the ten study sites, 19 cases show >80% reduction in pore-water concentrations in the short term with 10 of them showing >95% reduction. The pore-water concentrations are further reduced over time. After 15 years (long-term), >95% reduction is achieved for 18 of the 25 total cases. This suggests that in-situ AC amendment can be an effective solution to reduce the HOC pore-water concentration, which is indicative of the (bio)availability of the contaminants.

In some cases, however, the model predicts relatively low effectiveness of AC amendment for a target analyte. For example, the pore-water concentrations for p,p'-DDT at Lauritzen Channel are simulated to be reduced by only 34% after 15 years. As discussed in Tomaszewski et al. [6], this is due to the weathering of the compound by transformation reactions, locking up the residuals in the strongest sorption sites in the sediment. As a result, the sediment-water distribution coefficient (K_d) for p,p'-DDT was two orders of magnitude greater than the value for the other model compound, p,p'-DDD (dichlorodiphenyldichloroethane), at Lauritzen channel. In contrast to p,p'-DDT, the pore-water concentration for p,p'-DDD is predicted to be substantially reduced (i.e., by 98.7%) after 15 years. This shows that the effectiveness of the treatment is variable

depending on site characteristics and HOC properties, and limited benefit may be obtained when conditions are not favorable for AC amendment. Thus, for a compound that is very strongly sorbed and which may comprise only small amount of the total HOCs in the aqueous phase, the benefit of AC treatment is not as pronounced due to slow release by sediment and slow uptake by AC.

Generally, the percent reductions in pore-water concentrations tend to approach the endpoint values (i.e., at equilibrium) over time. For relatively less hydrophobic and smaller HOCs such as PAHs and less chlorinated PCB congeners, the percent reductions after 15 years are comparable to those at equilibrium. For relatively highly hydrophobic HOCs such as PCB 180 at Hunters Point Shipyard and p,p'-DDT at Lauritzen Channel, the percent reductions after 15 years are somewhat less than the equilibrium-based values, indicating a substantial time requirement for those compounds to desorb, diffuse into the AC and approach equilibrium.

Interestingly, the percent reduction in pore-water concentration after 15 years for benzo[a]pyrene (BaP) at River Tyne is greater than the equilibrium value. This is a result of very slow desorption kinetics of the compound at the site due to a high coal content of the sediment. The fraction of 30-d desorption fraction for BaP at River Tyne is only 0.01, which is much smaller than the average value of 0.69 for all 25 cases. As the desorption kinetics are extremely slow, the sediment desorption is a rate-controlling step for the overall mass transfer in this case. Only a small fraction of BaP is released to sediment pore-water even over an extended period of time (94% of total BaP mass resides in sediment after 15 years). The rest of the HOC mass transfer processes, the diffusion

through pore-water to the surface of AC and the diffusion into the AC particles, occur relatively faster, resulting in the depletion of the compound in sediment pore-water.

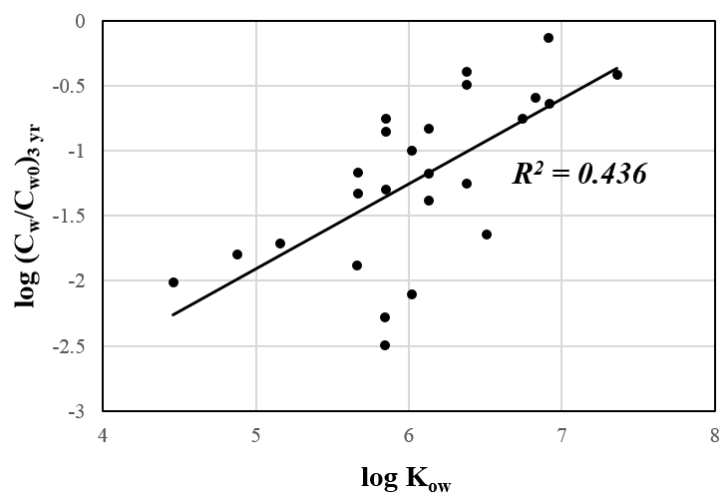
The time-dependent changes in relative pore-water concentrations for the ten study sites with a total of 25 simulation cases are plotted in **Fig. A.3 in Appendix A**. Considering the limited field experience with in-situ AC amendment, these simulated data provide a good reference for assessing the long-term effectiveness of the treatment for various combinations of site characteristics and target HOCs.

3.3. Correlation of effectiveness to site-specific variables and simple models

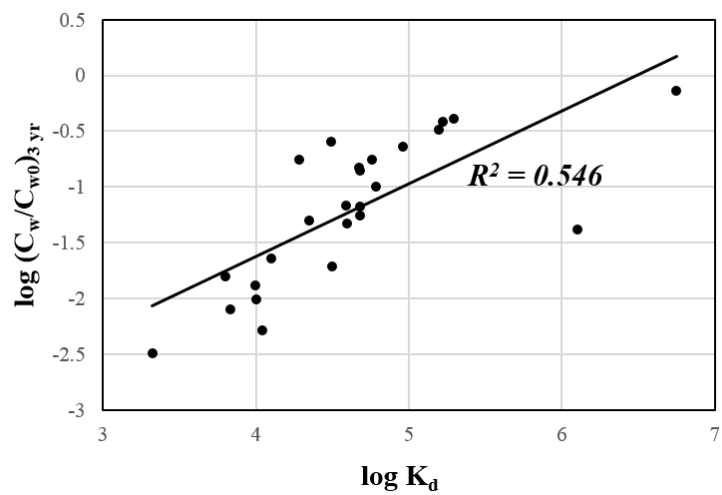
The model-predicted relative pore-water concentrations after 3 and 15 years (i.e., $(C_w/C_{w0})_{3yr}$ and $(C_w/C_{w0})_{15yr}$, respectively) are plotted against site-specific variables and values in **Figs. 2 and 3**. The values studied for correlation include the octanol-water partitioning coefficient (K_{ow}), the sediment-water distribution coefficient (K_d), the AC-water partitioning coefficient (K_{AC}), the equilibrium relative pore-water concentration ($(C_w/C_{w0})_{eq}$), TOC and BC contents, and the fraction of analyte desorbed from the sediment in 30 d.

Fig. 2. Correlation of $\log (C_w/C_{w0})_{3yr}$ with (a) $\log K_{ow}$, (b) $\log K_d$, (c) $\log K_{AC}$, (d) $\log (C_w/C_{w0})_{eq}$, (e) TOC content, (f) BC content, and (g) the fraction of 30-d desorption. $(C_w/C_{w0})_{3yr}$ and $(C_w/C_{w0})_{eq}$ denote the ratios of the pore-water concentration for the AC-amended sediment and the initial pore-water concentration 3 years after AC deployment and at equilibrium, respectively.

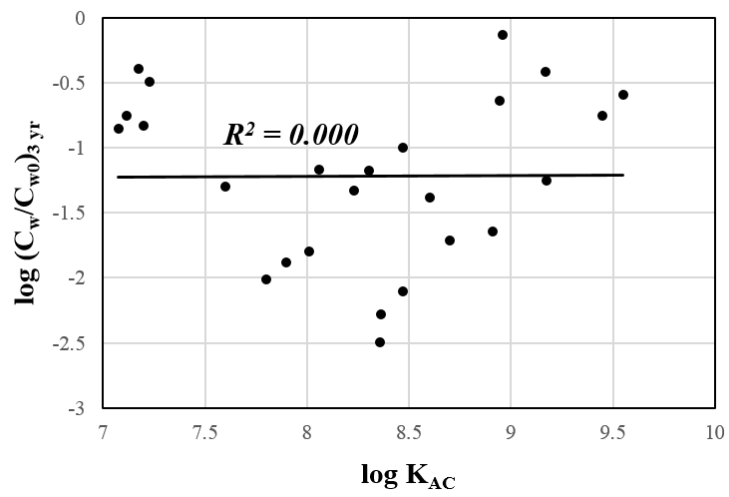
(a) $\log K_{ow}$



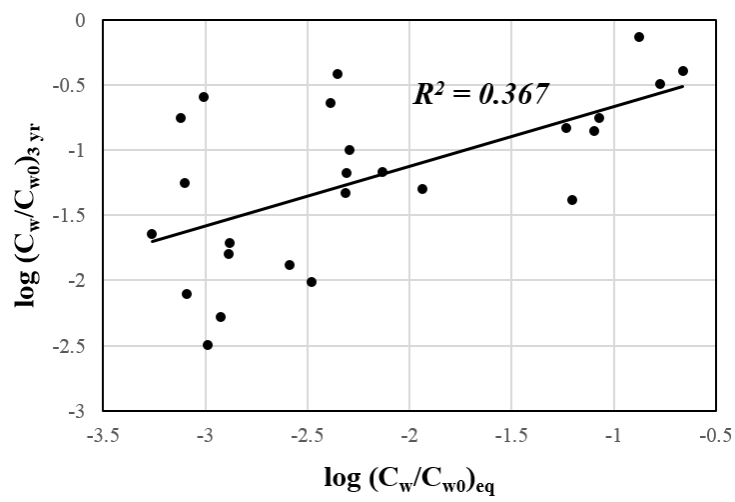
(b) $\log K_d$



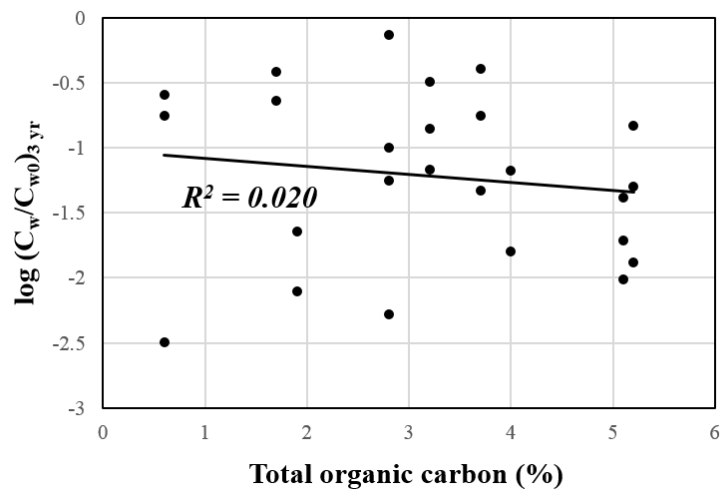
(c) $\log K_{AC}$



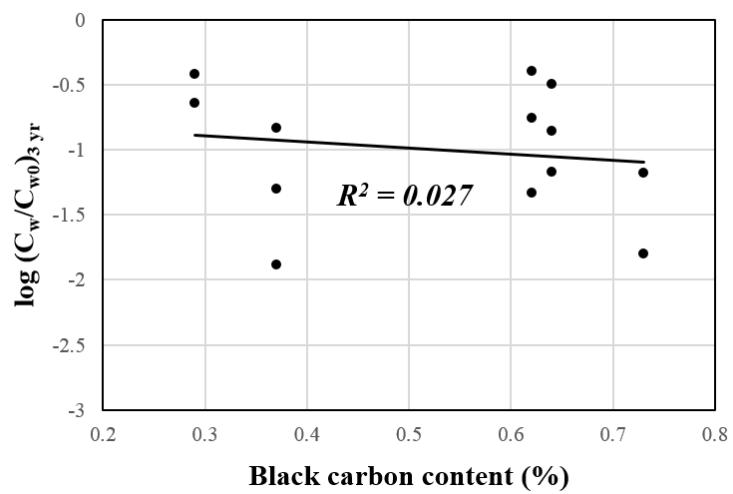
(d) $\log (C_w/C_{w0})_{eq}$



(e) TOC content



(f) BC content



(g) Fraction of 30-d desorption

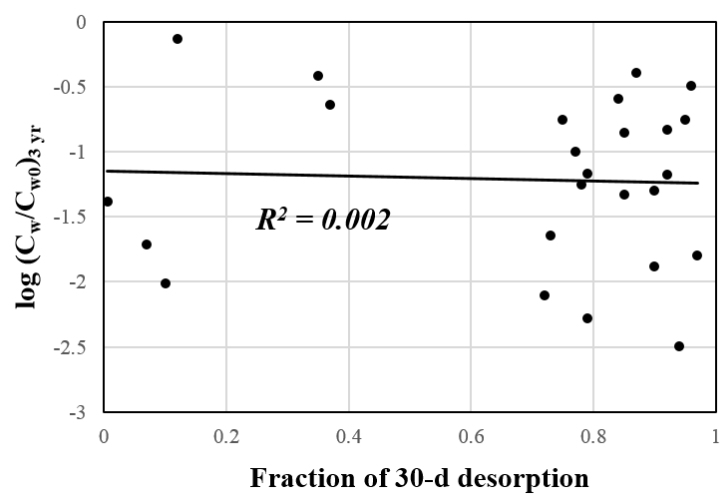
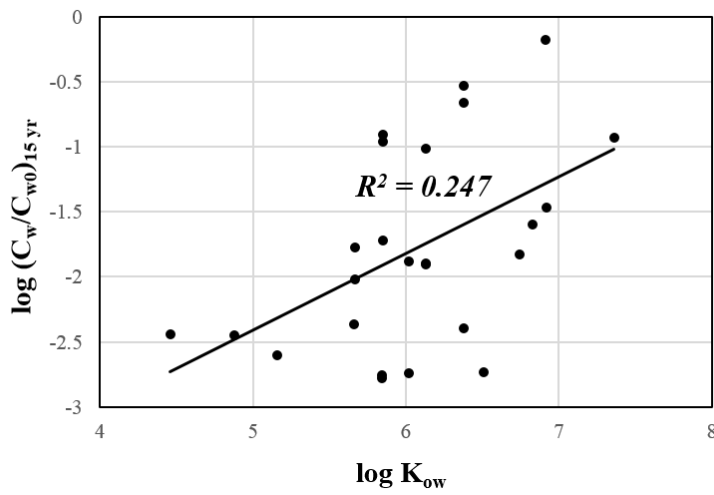
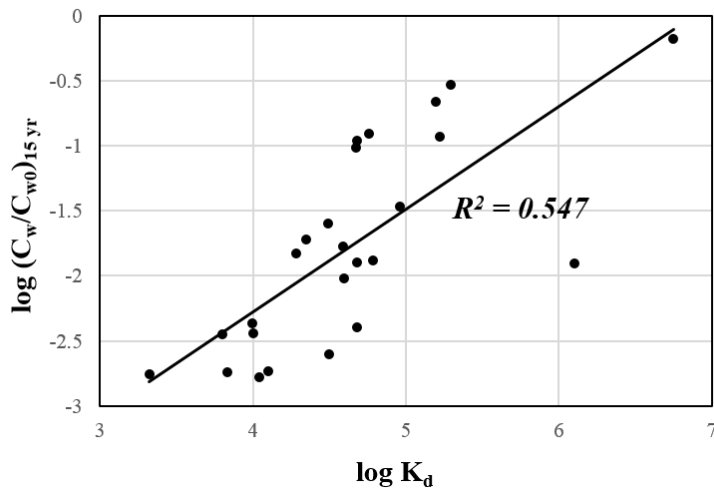


Fig. 3. Correlation of $\log (C_w/C_{w0})_{15\text{yr}}$ with (a) $\log K_{ow}$, (b) $\log K_d$, (c) $\log K_{AC}$, (d) $\log (C_w/C_{w0})_{eq}$, (e) TOC content, (f) BC content, and (g) the fraction of 30-d desorption. $(C_w/C_{w0})_{15\text{yr}}$ and $(C_w/C_{w0})_{eq}$ denote the ratios of the pore-water concentration for the AC-amended sediment and the initial pore-water concentration 15 years after AC deployment and at equilibrium, respectively.

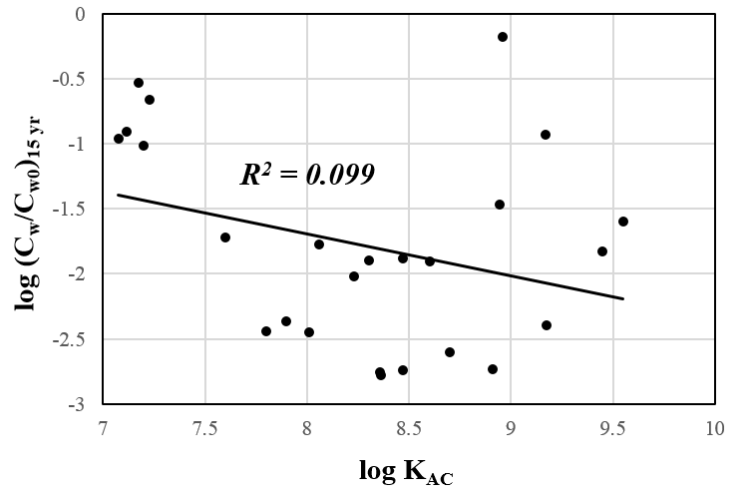
(a) $\log K_{ow}$



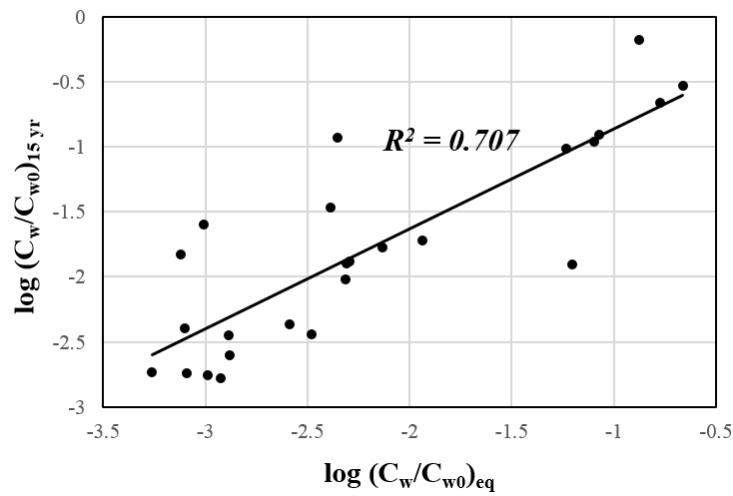
(b) $\log K_d$



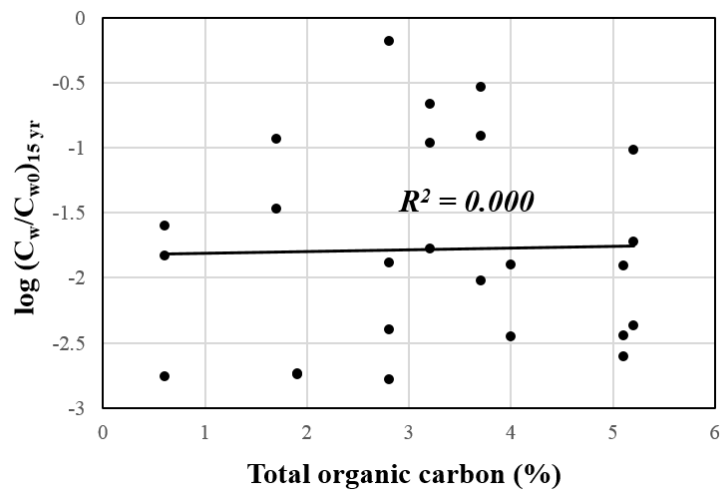
(c) $\log K_{AC}$



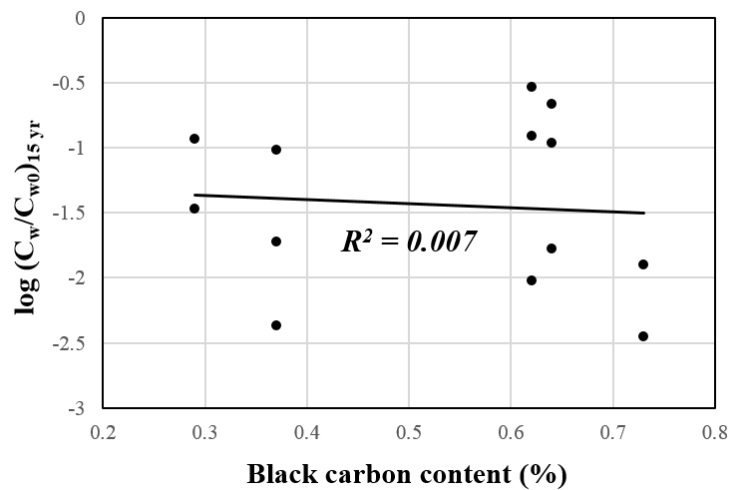
(d) $\log (C_w/C_{w0})_{eq}$



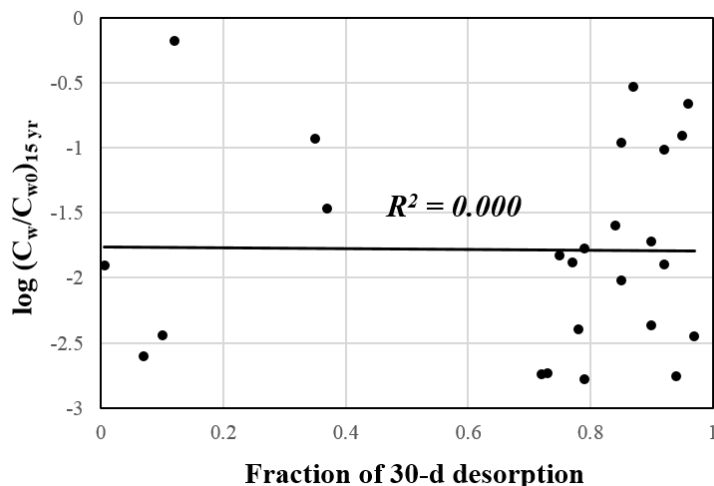
(e) TOC content



(f) BC content



(g) Fraction of 30-d desorption



The logarithm of K_{ow} values show negative correlation with the relative pore-water concentrations after 3 and 15 years. This is consistent with laboratory and field observations reported in the literature showing less efficiency of AC treatment for highly hydrophobic compounds [1, 4, 5, 9, 10]. The variations in the model-predicted results for HOCs having similar values of K_{ow} , however, indicate the significant contribution of the site-specificity on the overall effectiveness of AC amendment. The predicted $(C_w/C_{w0})_{15yr}$ values for tetra-chlorinated PCB congeners 47, 49, and 52, which have almost identical values of $\log K_{ow}$ (5.84 or 5.85), range two orders of magnitude. Still, the data in **Figs. 2a and 3a** suggest that the K_{ow} values may be a useful indicator to screen out the cases having the possibility of relatively poor effectiveness of AC amendment. In cases where predicted $(C_w/C_{w0})_{15yr}$ are greater than 0.2 (in other words, the relative reductions in pore-water concentration of less than 80%), the model compounds have $\log K_{ow}$ values greater than 6.3.

The logarithm of K_d values also show negative correlation with the relative pore-water concentrations. This indicates that the association of HOCs with sediment plays a

significant role in the overall HOC mass transfer in AC-treated sediments. High K_d values may be indicative of strong association of HOCs with sediment, resulting in resistance in HOC mass transfer from sediment, as discussed for the case of p,p'-DDT in the previous section.

To use the K_d values as an indicator of the feasibility of in-situ AC amendment, it is suggested to determine the value based on laboratory measurement. The K_d value may be calculated using the previously reported organic carbon-normalized partitioning coefficients (K_{oc}) and the sediment TOC, but studies have shown up to two orders of variation for the K_{oc} values for different types of sediment [28]. Therefore, the K_{oc} -based calculation may not represent the site-specific association of HOCs with the field sediment. All K_d values obtained from the literature in the current study were determined from laboratory measurements.

The equilibrium relative pore-water concentrations, $(C_w/C_{w0})_{eq}$, show positive correlation with the relative pore-water concentrations after 3 and 15 years. As expected, the 15-year relative pore-water concentrations $((C_w/C_{w0})_{15yr}; R^2=0.707)$ show better correlation with the $(C_w/C_{w0})_{eq}$ than the 3-year values $((C_w/C_{w0})_{3yr}; R^2=0.367)$ as the HOC mass transfer proceeds towards equilibrium over time. The results suggest that the equilibrium-based calculations are useful for screening of the feasibility of AC amendment, although kinetics also play a significant role in the long term as well as in the short term. As shown in eq. (5), the K_d and K_{AC} values should be obtained to calculate the equilibrium values. In addition to the K_d value, K_{AC} value is also suggested to be determined in a site-specific manner. Although the AC partitioning coefficients (K_{AC}) for single solutes are available for many HOCs in the literature, it has been shown that the

apparent K_{AC} values in AC-amended sediments are sometimes less than the reported values of K_{AC} by an order of magnitude or more, primarily because of the competitive effect among HOCs in the sediment [7, 17, 29]. Therefore, to obtain the calibrated equilibrium-based values, site-specific determination of the partitioning coefficients through laboratory measurements may be needed.

There are no meaningful correlations among $\log K_{AC}$, TOC and BC contents, and fraction of 30-d desorption to the relative pore-water concentrations. The absence of a correlation among those parameters with the simulation results suggest that these parameters are not appropriate for use as a sole indicator of the effectiveness of AC amendment. However, the results do not necessarily mean that the parameters are not relevant to the effectiveness. It is likely that effects of those parameters are masked by other variables that are associated with the parameters, or the parameters have relatively small impact to the overall effectiveness. Plausible explanations of the absence of correlation with the simulation results for each of those parameters are discussed in **Appendix A**.

4. Conclusions

An HOC mass transfer model is developed that can accommodate plausible field heterogeneity of AC mixing into sediment. Based on the AC mixing heterogeneity observed in a pilot-scale study at Hunters Point Shipyard, the model is systematically organized to account for a large scale (around 10 cm) and millimeter-scale vertical heterogeneity of AC mixing. The new model is used to simulate the effectiveness of in-situ AC amendment for ten sites having different site characteristics and HOCs of

concern. The simulation results show a significant short- and long-term benefit of AC amendment for most of the tested cases. The simulated relative pore-water HOC concentrations 3 and 15 years after AC deployment show negative correlation with the octanol-water partitioning coefficients and the sediment-water distribution coefficients and positive correlation with the equilibrium-based relative pore-water HOC concentrations. These variables are likely to be useful to assess the feasibility of AC amendment at a screening level. Other variables, i.e., the AC-water partitioning coefficient, TOC, black carbon content, and the fraction of 30-d desorption do not solely show a direct relationship with the simulated relative pore-water HOC concentrations.

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